METHOD OF PRODUCING AND USING MATERIALS WHICH ARE REINFORCED AGAINST IMPACT AND WHICH CONTAIN BLOCK COPOLYMERS THAT ARE OBTAINED BY MEANS OF CONTROLLED RADICAL POLYMERIZATION IN THE PRESENCE OF NITROXIDES

Field of the Invention

The present invention relates to the field of materials reinforced against impacts and particularly to materials which are both transparent and reinforced against impacts and more particularly to materials reinforced against impacts using a block copolymer.

Background of the Invention

The present invention discloses the preparation and the use in brittle thermoplastic polymer matrices of block copolymers obtained by controlled radical polymerization in the presence of stable nitroxides, the materials thus obtained exhibiting improved properties of impact strength.

Impact-resistant thermoplastic resins are conventionally obtained by hot blending an impact-reinforcing additive, resulting from the stages of coagulating, dehydrating and drying an elastomer latex, with the particles of the “hard” polymer or thermoplastic resin, which results in what is known as an alloy, from which it is possible to obtain articles shaped by extrusion, injection molding or compression.

Summary of the Invention

~~The~~ Applicant ~~Company~~ has just found a novel class of polymer materials which are both transparent and impact-resistant and a novel way of preparing impact-resistant polymer materials.

Brief Description of the Drawings

Figure 1 shows the results of the traction-elongation test.

Detailed Description of the Invention

The first subject matter of the present invention is transparent and impact-resistant polymer materials composed of a brittle matrix (I), representing from 0 to 95% by weight of the total weight of the materials of the invention, in which is dispersed a block copolymer (II) of general formula $B-(A)_n$. Advantageously, the portion of the brittle matrix is between 10 and 85% by weight.

The materials of the invention can additionally comprise other impact-reinforcing additives, such as those of the Durastrength™ or Metablend™ trade mark, and the like. Generally, the brittle matrix (I) exhibits a glass transition temperature (Tg) of greater than 0°C. Mention may in particular be made, among brittle matrices which it is important to reinforce against impacts, of materials based on poly(methyl methacrylate), on polystyrene, on poly(vinylidene fluoride), on polyesters, on polycarbonate, on poly(vinyl chloride), on polyamide, on polyepoxide, on polyethylene or on polyacrylonitrile, or their copolymers.
The brittle matrix is preferably a polymethacrylate.

The block copolymers of the invention correspond to the general formula $B-(A)_n$, n being a natural number of greater than two, preferably between 2 and 20 and preferably between 2 and 8; where B represents a polymer block composed of the sequence of monomer units which can be polymerized by the radical route, the overall Tg of which is less than 0°C. The average molar mass of the block B is greater than 5000 g/mol, preferably greater than 20 000 g/mol and more preferably still greater than 50 000 g/mol.

A is a polymer block composed of a sequence of monomer units which can be polymerized by the radical route, the overall Tg of which is greater than 0°C. The average molar mass of each block A is between 10 000 g/mol and 10^6 g/mol, preferably between 10 000 g/mol and 200 000 g/mol and preferably between 20 000 and 100 000 g/mol.

The relative lengths of the blocks A and B are chosen such that n*Mn(A)/(n*Mn(A)+Mn(B)) is between 0.5 and 0.95, preferably between 0.6 and 0.8, and such that Mn(B) is greater than or equal to the mean entanglement length of the block B, where Mn denotes the number-average molecular mass of the polymer.

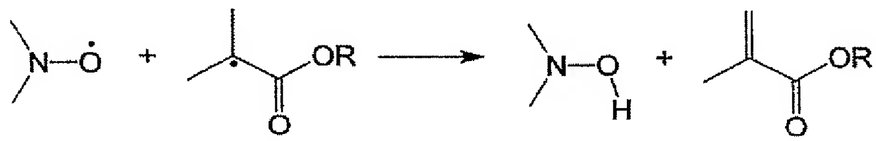
According to the invention, the block copolymer (II) exhibits a polydispersity index of between 1.5 and 3, advantageously of between 1.8 and 2.7 and preferably of between 1.9 and 2.5. On the other hand, the block B exhibits a polydispersity index of less than 2.

Generally, A represents at least 50% by weight of the total weight of the copolymer (II) and preferably between 60 and 95%.

In particular, B is a polyacrylate with a glass transition temperature of less than 0°C; preferably, B will comprise butyl acrylate units. A is a polymer compatible with the matrix to be reinforced. By way of indication, in order to reinforce poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVDF) or poly(vinyl chloride) (PVC), PMMA will be chosen for A. In order to reinforce polyesters, such as poly(butylene terephthalate) or poly(ethylene terephthalate), or epoxys, A will preferably be chosen from polymethacrylates comprising glycidyl methacrylate or methacrylic acid units and, in order to reinforce polystyrene, PS will preferably be chosen for A.

Another subject-matter of the invention is a process for the preparation of the transparent and impact-resistant materials of the invention. This process is based on the "controlled radical polymerization" polymerization technique based on the use of stable nitroxides. The general synthetic scheme is as follows: in a first step, the block B, with a flexible or elastomeric nature, is prepared by polymerization in the presence of a well chosen nitroxide and, in a second step, by using the block B as polymerization initiator, the branches A, with a stiff or thermoplastic nature, are prepared.

It is known that stable nitroxides can result in the formation of block copolymers by controlled radical polymerization (WO 9624620, WO 2000071501 A1 20001130, EP 1142913 A1 20011010). By virtue of certain families of nitroxides described in the abovementioned patents, block copolymers incorporating units as difficult to control by the conventional radical route as acrylates are described. In the case of methacrylates, certain limitations well known to a person skilled in the art appear, such as the transfer reaction with the nitroxide (eq. 1), which brings about a premature loss in the control of the polymerizations:



(eq.1)

However, starting from a first block controlled by the nitroxide, it is possible to reinitiate a radical methacrylate polymerization, which will be limited in its living nature but will still result in a block copolymer.

The limitations of the living nature are reflected by a broadening of the polydispersity of the copolymer block, of between 1.5 and 2.5, and the Applicant Company has discovered that this had an effect on the morphology of the block copolymer.

This is because monodisperse block copolymers will experience transitions in morphology for copolymer block compositions which are very specific (cf. G. Holden et al. in "*Thermoplastic elastomers*", 2nd edition, Carl Hanser Verlag, Munich, Vienna, New York, 1996). For this reason, when the proportion of the thermoplastic block increases, the morphology changes towards a topology where the continuous phase is the thermoplastic phase.

As long as this situation is not reached, the block copolymer cannot be homogeneously blended with a matrix compatible with the thermoplastic block. For this reason, the blend becomes

opaque and the mechanical properties thereof are very poor.

As the two-stage synthesis according to any one process for the polymerization (mass, solvent, emulsion, suspension) of copolymer block in the presence of nitroxides is very simple to carry out, it was essential to find the compositions or the methods of synthesis which result in copolymers which can be compatibilized with thermoplastic matrices. The Applicant Company has discovered that, for compositions comprising between 50% and 95% of thermoplastic phase, preferably between 60% and 85% of thermoplastic phase, the morphology of the copolymers obtained by controlled radical polymerization in the presence of nitroxides was compatible with a good mixture of the copolymer in brittle thermoplastic matrices.

Furthermore, unlike the document JP2000198825 A 20000718, in which the authors claim the use of block copolymers obtained by controlled radical polymerization in the presence of copper salt with a low polydispersity index (PI<1.5), the Applicant Company has found that, by virtue of the controlled radical polymerization in the presence of nitroxide, the polymerization of the thermoplastic block could take place at the same time as the polymerization of the matrix and that it was not necessary to isolate the block copolymer beforehand. Thus, starting from a first block functionalized by nitroxides, it is possible to initiate thermoplastic chains at the same time as other chains are initiated by conventional initiators or by thermal initiation. There are two advantages to this:

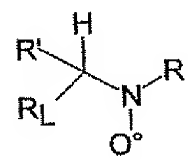
1 - If the thermoplastic matrix to be reinforced against impact has the same composition as the thermoplastic block of the copolymer, the reinforced material is obtained directly.

2 - If another matrix has to be reinforced, the fact of adding homopolymers to the block copolymer makes it possible to fluidify the copolymer, which, if not, exhibits too excessive a viscosity to be converted by extrusion without undergoing decomposition.

~~The~~ Applicant ~~Company~~ thus claims a process for the

manufacture of block copolymers which are compatible with thermoplastic matrices and the use of these block copolymers in the manufacture of these resins which are more resistant to impact.

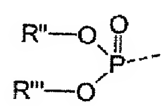
In particular, the process according to the invention consists of the synthesis of the copolymers in the presence of nitroxides (III):



(III)

- where R′ and R, which are identical or different, optionally connected so as to form a ring, are alkyl groups having between 1 and 40 carbon atoms optionally substituted by hydroxyl, alkoxy or amino groups; in particular, R and R′ will be tert-butyl groups;

- and where R_L is a monovalent group with a molar mass of greater than 16 g/mol; in particular, R_L will be a phosphorus group and more particularly a phosphonate group of formula:



- where R″ and R‴, which are identical or different, optionally connected so as to form a ring, are alkyl groups having between 1 and 40 carbon atoms optionally substituted by hydroxyl, alkoxy or amino groups; in particular R″ and R‴ will be ethyl groups.

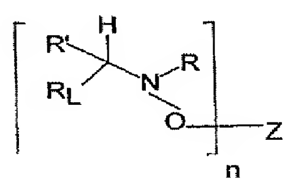
In particular, the block copolymers are of general formula $B-(A)_n$, where B represents a polymer block composed of the sequence of monomer units which can be polymerized by the radical route in the presence of nitroxides (III) and for which the overall Tg is less than 0°C. The average molar mass of the block B is between 3000 g/mol and 10^6 g/mol, preferably between 5000 g/mol and 200 000 g/mol and preferably between 5000 and 100 000 g/mol;

A is a block of the polymer composed of a sequence of monomer units which can be polymerized by the radical route in the presence of nitroxides (III) and for which the overall Tg is greater than 0°C. The average molar mass of each block A is between 10 000 g/mol and 10^6 g/mol, preferably between 10 000 g/mol and 200 000 g/mol and preferably between 20 000 and 100 000 g/mol, where n is a natural number greater than two, preferably of between 2 and 20 and preferably between 2 and 8.

The relative lengths of the blocks A and B are chosen such that n*Mn(A)/(n*Mn(A)+Mn(B)) is between 0.5 and 0.95, preferably between 0.6 and 0.8, and such that Mn(B) is greater than or equal to the mean entanglement length of the block B. The polydispersity of the block copolymer obtained is between 1.5 and 3, preferably between 1.8 and 2.7 and more preferably from 1.9 to 2.5.

The process is characterized in that it consists:

1) firstly, in preparing, according to a conventional polymerization recipe, the first block B by mixing the monomer(s) with an alkoxyamine of general formula (IV):



(IV)

where Z is a polyvalent radical carrying terminal functional groups of styryl or acryloyl type, the other radicals having the same meanings as above,
nitroxide (III) being added to the mixture in a proportion ranging from 0 to 20 mol% with respect to the moles of alkoxyamine functional groups (one alkoxyamine contributes n alkoxyamine functional groups).

The polymerization is carried out at temperatures ranging from 60 to 250°C, preferably from 90 to 160°C, for pressures ranging from 0.100 bar to 80 bar, preferably from 0.5 bar to 10 bar.

The polymerization has to be controlled and the latter

will preferably be halted before 99% conversion, preferably before 90% conversion. The block B thus obtained is either used with the residual monomers or is purified from the monomers by distillation or washing and drying with a solvent which is immiscible with B and miscible with the monomers used.

2) Secondly, the process consists in diluting the first block B obtained in the mixture of monomers intended to form the blocks A. Between 0 and 100 molar equivalents of conventional radical polymerization initiator (of the Luperox™ or azo compound type, for example AZDN™) are added to this mixture. The choice of this ratio depends on the viscosity/impact-reinforcing compromise which it is desired to have.

The polymerization is carried out at temperatures ranging from 60 to 250°C, preferably from 90 to 160°C, for pressures ranging from 0.100 bar to 80 bar, preferably from 0.5 bar to 10 bar.

The conversion of the monomer varies from 10 to 100% and the polymer obtained is separated from the residual monomers by evaporation under vacuum at temperatures ranging up to 250°C and preferably 200°C.

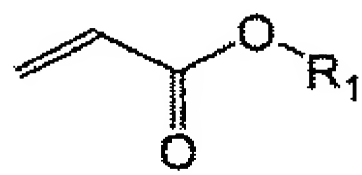
3) Thirdly,

- either the material obtained is extruded in the presence of the brittle matrix which it is desired to see reinforced against impact: mention may in particular be made of PMMA, polyesters of PET or PBT type, polystyrene, PVDF, polyamides, polycarbonates, PVC and the like. This extrusion stage can also involve other additives, in particular impact additives, such as those of the Durastrength™ or Metablend™ trade mark,
- or else the material obtained is diluted in a mixture of monomers which is itself subsequently polymerized. Mention may be made, for example, of styrene, MMA, epoxides, mixtures of diols and

of diacid, or precursors of polyamides (lactam or mixtures, diamine, diacids),

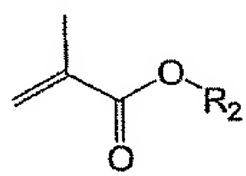
- it is also possible to use the material as an impact-resistant resin without blending.

A person skilled in the art knows how to choose his monomers according to the block desired. Mention may be made, among the monomers chosen, pure or as a mixture, of acrylic monomers of general formula:



where R^1 is a hydrogen atom or a linear, cyclic or branched alkyl comprising from 1 to 40 carbon atoms which is optionally substituted by a halogen atom or a hydroxyl (-OH), alkoxy, cyano, amino or epoxy group.

Another family of monomers of choice is composed of methacrylic monomers of general formula:



where R_2 has the same meaning as R_1.

Another possible monomer is acrylonitrile, styrene derivatives, dienes and generally any monomer carrying a vinyl bond which can be polymerized by the radical route.

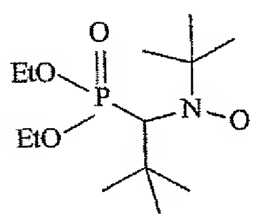
The materials of the invention can be used in various fields, such as the automobile industry or the construction industry. They make it possible to manufacture impact-resistant shaped articles, in particular sheets, and very particularly sheets of use in forming thermoformed bathroom fittings, such as bath tubs, sinks, shower trays, basins, shower stalls and the like.

These shaped articles exhibit an improved impact strength while retaining good mechanical properties, in particular with regard to flexion (high modulus), that is to say a degree of stiffness.

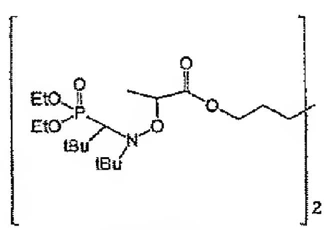
The following examples illustrate the invention without limiting the scope thereof.

Examples:

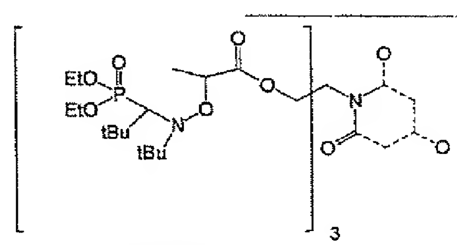
The stable free radical used in the examples and referenced SG1 corresponds to the following formula:



The alkoxyamines DIAMS and TRIAMS mentioned in the examples correspond to the following formulae:



DIAMS



TRIAMS

I. First series: Reinforcement against impacts of a PMMA matrix by a B-(A)$_n$ copolymer with n = 2 or 3

I.1 Preparation of the copolymers:

The general procedure for syntheses and for characterizations is described below.

The syntheses are carried out in two stages in a steel reactor with a working capacity of 9 liters. The starting media are systematically degassed by vacuum/nitrogen cycles before being introduced into the reactor, which is preheated to the reaction temperature.

The control of the polymerization of butyl acrylate, for example, in the presence of the alkoxyamines 1 or 2 denoted

respectively by DIAMS and TRIAMS was optimized at a temperature T = 115°C and in the presence of an excess of free SG1 of 7 mol% per alkoxyamine functional group. Conversion was limited to 50%, so as to retain a good living nature of the PBuA-SG1 macroinitiators obtained, the residual monomer subsequently being removed by a stripping stage (70°C under vacuum for 2 hours).

In a second stage, the di- or trifunctional macroinitiators thus obtained were allowed to reinitiate the polymerization of MMA at 120°C under pressure, so as to prepare triblock and star block copolymers. It is important to note that the conversion of MMA is limited because of disproportionation reactions between the nitroxide and the growing chains. Starting from synthesis No. 2, a rise in temperature in stationary phases between 85 and 120°C was opted for, which made it possible to push back this limit from 20 to 45%.

The operating conditions for the syntheses of the block B functionalized with a stable free radical, SG1, are summarized in table 1 (Tab 1).

Table 1: Synthesis of PBuA-SG1 macroinitiators

	DIAMS/TRIAMS*		SG1		BuA		Mn (th)
	w (g)	C (mol/l)	w (g)	C (mol/l)	w (g)	C (mol/l)	
PBuAFLOPIL6 (DIAMS)	59.7073	1.49×10^{-2}	3.1907	2.09×10^{-3}	3600	6.98	60 000
PBuAFLOPIL7 (DIAMS)	58.0488	1.49×10^{-2}	2.7919	2.09×10^{-3}	3500	6.98	60 000
PBuAFLOPIL8 (DIAMS)	54.0488	1.49×10^{-2}	2.7919	2.09×10^{-3}	3500	6.98	60 000
PBuAFLOPIL9 (TRIAMS)	69.9200	0.99×10^{-2}	2.8716	2.09×10^{-3}	3600	6.98	90 000

The operating conditions relating to the preparation of 4 block copolymers, poly(butyl acrylate) for block B and

poly(methyl methacrylate) for block A, are summarized in table 2.

Table 2: Syntheses of the PBuA-SG1 copolymers

	PBuA-SG1		MMA		Ethylbenzene		Mn (f=1) (PMMA)
	w (g)	C (mol/l)	w (g)	C (mol/l)	w (g)	C (mol/l)	
FLOPIL6	1800	9.81×10^{-3}	6250	7.16	1780 (20%)	1.92	73 000
FLOPIL7	1800	1.29×10^{-3}	6420	8.21	830 (10%)	1.00	64 000
FLOPIL8	1100	5.31×10^{-3}	6750	8.25	840 (10%)	0.97	155 200
FLOPIL9	1100	3.23×10^{-3}	6750	8.25	840 (10%)	0.97	245 500

I.2 Preparation of the reinforced matrix:

The blends composed of PMMA and of copolymers which reinforce against impacts are prepared by melt extrusion.

I.3 Characterizations

The molar masses and their distribution were determined by steric exclusion chromatography (SEC), by universal calibration using polystyrene standards and the Mark-Houwink coefficients of PBuA for the PBuA-SG1 macroinitiators and of PMMA for the copolymers.

The composition of the copolymers in PBuA and PMMA was determined by proton NMR. The results obtained are given in table 3 (Tab 3) as regards the block B and in table 4 (Tab 4) as regards the copolymers.

Table 3: Characteristics of the macroinitiators

	BuA conversion %	Mn (theoretical) (g/mol)	Mn (SEC) (g/mol)	Mw (SEC) (g/mol)	PI

PBuAFLOPIL6	35	21 000	21 000	31 700	1.50
PBuA-FLOPIL7	50	30 000	17 800	55 400	3.11
PBuA-FLOPIL8	47	28 200	25 300	35 000	1.38
PBuA-FLOPIL9	50	45 000	28 000	44 000	1.57

Table 4: Characteristics of the copolymers

	MMA conversion %	Mn (th) (g/mol)	Mn (SEC) (g/mol)	Mw (SEC) (g/mol)	PI	%PMMA by weight
FLOPIL 6	20	35 600	44 900	124 200	2.70	68
FLOPIL 7	35	40 000	77 400	170 760	2.20	70
FLOPIL 8	44	93 600	100 200	240 600	2.40	80
FLOPIL 9	40	138 200	87 230	245 900	2.8	77

The mechanical properties were evaluated by the well-known traction-elongation test. The results are illutrated by figure No. 1.

II. Second series: In situ preparation of a PMMA reinforced against impacts by the polymerization of a methyl methacrylate/macroinitiator based on butyl acrylate and on styrene mixture (syrup), either by the "cast sheet" technique or continuously

II.1 Cast sheet

Stage 1:

Preparation of butyl acrylate/styrene (83/17) copolymer by polymerizing by up to 69% a mixture comprising 7.2 kg of butyl acrylate, 800 g of styrene, 51 g of TRIAMS and 1.5 g of free SG1. The copolymer is recovered by evaporation of the volatile components and then dissolution in 8 kg of methyl methacrylate.

The macroinitiator obtained exhibits the following characteristics: 17% by weight of styrene, Mn = 70 000 g/mol, Mw = 142 000 g/mol.

Stage 2:

The formulation of the methyl methacrylate syrup employed is as follows:

A variable concentration of macroinitiator obtained according to stage 1: either 2% or 5% or 7.5% or 10% or 20% by weight of the total weight of the mixture.
550 ppm of Luperox 331-80M.
0.2% by weight of the total weight of the mixture of maleic anhydride.
21 ppm of γ-terpinene.
The sheets are introduced into an oven and are heated at 90°C for approximately 16 hours and, in postpolymerization, at 125°C for 2 hours.
These examples show (see table 5, Tab 5) that the incorporation of a block copolymer in a PMMA matrix of cast sheet type contributes a significant reinforcement against impact which is greater than the best current commercial reference.

Table 5: Results

Amount of PBuA	Appearance	Haze	Residual MMA	Resilience * (in kJ.m^2)
2%	+++	1.18	3.65%	1.35±0.06
5%	+++	1.59	3.32%	1.78±0.16
7.5%	+++	2.43	3.87%	2.81±0.18
10%	+++	3.52	3.45%	3.62±0.25
20%	+++	5.94	2.38%	6.23±0.25

+++: No bloom, no bubbles, translucent, glossy, smooth.
*: The impact results were produced on notched test specimens with a non-instrument-controlled Charpy device and a 1 joule hammer and at a velocity of 2.9 m.s^{-1}.
For reference, the resilience of an unreinforced cast sheet and that of a cast sheet of commercial impact grade were measured, which have values of 1.35±0.03 kJ.mol^{-1} and 1.59±0.03 kJ.mol^{-1} respectively.

They also illustrate the fact that the block copolymers obtained by virtue of the chemistry of the nitroxides of the

invention can be introduced in situ during the polymerization of the matrix.

II.2 Continuous polymerization

Use is made in this example of an arrangement composed of two reactors in cascade. One is maintained at -40°C and is used to feed the second with polymerization syrup. The second reactor is the polymerization reactor proper. The polymerization temperature is greater than 160°C. The monomer syrup is introduced into the polymerization reactor with a flow rate of 8 kg/h. As soon as a level of solid of the order of 60% is obtained, the polymerization medium is pumped continuously to a degassing extruder at a temperature of 230°C. The material is granulated after cooling in a water vat.

The monomer syrup used is as follows (as proportion by weight):
Poly(butyl acrylate); it is the copolymer Flopil 9 described above: 15%.
Ethyl acrylate: 0.6%.
Di(tert-dodecyl) disulfide: 100 ppm.
Dodecyl mercaptan: 0.34%.
Luperox 531: 180 ppm.
The maximum polymerization temperature achieved is 178°C.
The granules obtained have the final composition:

82.5% PMMA
17.3% acrylate (butyl and ethyl)
0.2% residual MMA.

Mn = 30 000 g/mol (PMMA standard)
Mw = 85 000 g/mol (PMMA standard)

The measurements of the yield stress of a standard PMMA, of a PMMA reinforced against impacts and of the material prepared according to the invention, carried out by compressive tests on cylindrical test specimens according to Standard ISO 604, made it possible to derive the following values:
Standard PMMA (MC31): 130 MPa

PMMA reinforced against impacts (commercial product: M17T): 98 MPa

Reinforced PMMA according to the invention: 96 MPa.

The comparison of these results shows that the product according to the invention has a ductile behavior equivalent to a standard impact grade of PMMA.

Although the invention has been described in conjunction with specific embodiments, it is evident that many alternatives and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, the invention is intended to embrace all of the alternatives and variations that fall within the spirit and scope of the appended claims. The foregoing references are hereby incorporated by reference.

~~ANNEXES~~

~~Table 1: Synthesis of PBuA-SG1 macroinitiators~~

	~~DIAMS/TRIAMS*~~		~~SG1~~		~~BuA~~		~~Mn (th)~~
	~~w (g)~~	~~C (mol/l)~~	~~w (g)~~	~~C (mol/l)~~	~~w (g)~~	~~C (mol/l)~~	
~~PBuAFLOPIL6 (DIAMS)~~	~~59.7073~~	~~1.49×10^{-2}~~	~~3.1907~~	~~2.09×10^{-3}~~	~~3600~~	~~6.98~~	~~60 000~~
~~PBuAFLOPIL7 (DIAMS)~~	~~58.0488~~	~~1.49×10^{-2}~~	~~2.7919~~	~~2.09×10^{-3}~~	~~3500~~	~~6.98~~	~~60 000~~
~~PBuAFLOPIL8 (DIAMS)~~	~~54.0488~~	~~1.49×10^{-2}~~	~~2.7919~~	~~2.09×10^{-3}~~	~~3500~~	~~6.98~~	~~60 000~~
~~PBuAFLOPIL9 (TRIAMS)~~	~~69.9200~~	~~0.99×10^{-2}~~	~~2.8716~~	~~2.09×10^{-3}~~	~~3600~~	~~6.98~~	~~90 000~~

~~Table 2: Syntheses of the PBuA-SG1 copolymers~~

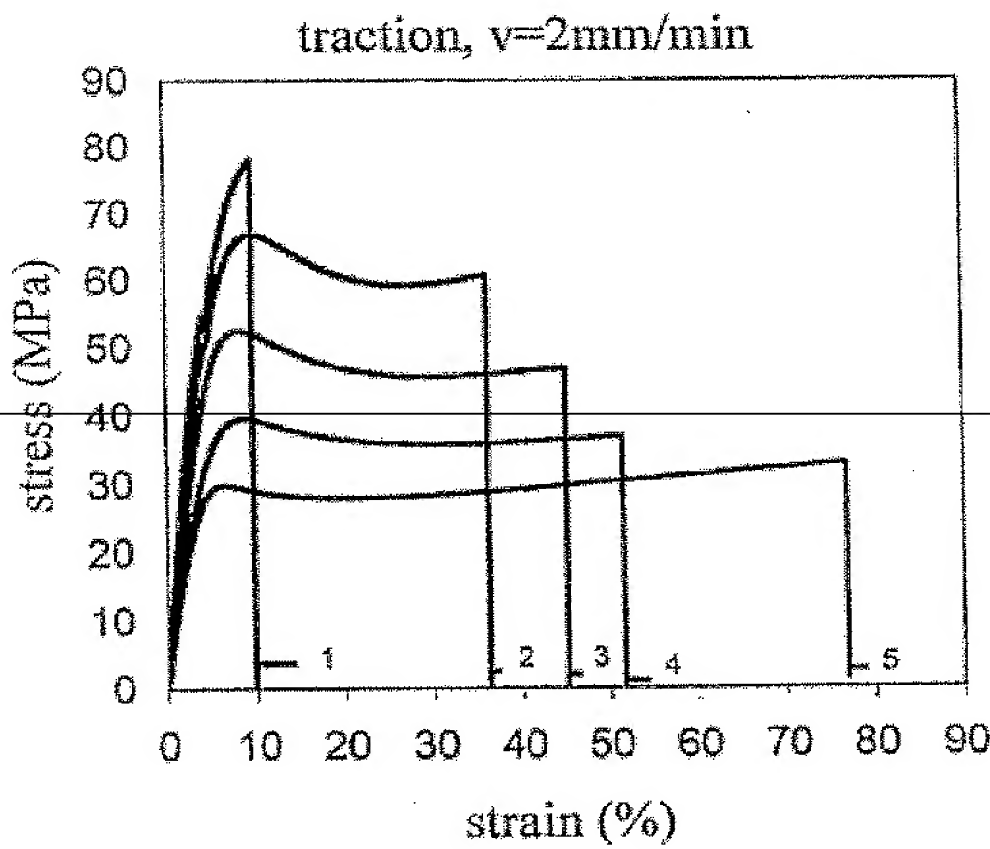
	~~PBuA-SG1~~		~~MMA~~		~~Ethylbenzene~~		~~Mn (f=1) (PMMA)~~
	~~w (g)~~	~~C (mol/l)~~	~~w (g)~~	~~C (mol/l)~~	~~w (g)~~	~~C (mol/l)~~	
~~FLOPIL6~~	~~1800~~	~~9.81×10^{-3}~~	~~6250~~	~~7.16~~	~~1780 (20%)~~	~~1.92~~	~~73 000~~
~~FLOPIL7~~	~~1800~~	~~1.29×10^{-3}~~	~~6420~~	~~8.21~~	~~830 (10%)~~	~~1.00~~	~~64 000~~
~~FLOPIL8~~	~~1100~~	~~5.31×10^{-3}~~	~~6750~~	~~8.25~~	~~840 (10%)~~	~~0.97~~	~~155 200~~
~~FLOPIL9~~	~~1100~~	~~3.23×10^{-3}~~	~~6750~~	~~8.25~~	~~840 (10%)~~	~~0.97~~	~~245 500~~

~~Table 3: Characteristics of the macroinitiators~~

	~~BuA conversion %~~	~~Mn (theoretical) (g/mol)~~	~~Mn (SEC) (g/mol)~~	~~Mw (SEC) (g/mol)~~	~~PI~~
~~PBuAFLOPIL6~~	~~35~~	~~21 000~~	~~21 000~~	~~31 700~~	~~1.50~~
~~PBuA-FLOPIL7~~	~~50~~	~~30 000~~	~~17 800~~	~~55 400~~	~~3.11~~
~~PBuA-FLOPIL8~~	~~47~~	~~28 200~~	~~25 300~~	~~35 000~~	~~1.38~~
~~PBuA-FLOPIL9~~	~~50~~	~~45 000~~	~~28 000~~	~~44 000~~	~~1.57~~

~~Table 4: Characteristics of the copolymers~~

	~~MMA conversion %~~	~~Mn (th) (g/mol)~~	~~Mn (SEC) (g/mol)~~	~~Mw (SEC) (g/mol)~~	~~PI~~	~~%PMMA by weight~~
~~FLOPIL6~~	~~20~~	~~35 600~~	~~44 900~~	~~124 200~~	~~2.70~~	~~68~~
~~FLOPIL7~~	~~35~~	~~40 000~~	~~77 400~~	~~170 760~~	~~2.20~~	~~70~~
~~FLOPIL8~~	~~44~~	~~93 600~~	~~100 200~~	~~240 600~~	~~2.40~~	~~80~~
~~FLOPIL9~~	~~40~~	~~138 200~~	~~87 230~~	~~245 900~~	~~2.8~~	~~77~~



~~**Figure 1 : Traction-elongation test**~~

~~*Key:*~~

~~(1) Black, V825 (conventional PMMA matrix)~~

~~(2) Blue, 25% of Flopil 9~~

~~(3) Red, 50% of Flopil 9~~

~~(4) Green, 75% of Flopil 9~~

~~(5) Pink, 100% of Flopil 9~~

~~Table 5~~

~~A. RESULTS OBTAINED:~~

~~Amount of PBuA~~	~~Appearance~~	~~Haze~~	~~Residual MMA~~	~~Resilience* (in kJ.m^{-2})~~
~~2%~~	~~+++~~	~~1.18~~	~~3.65%~~	~~1.35±0.06~~
~~5%~~	~~+++~~	~~1.59~~	~~3.32%~~	~~1.78±0.16~~
~~7.5%~~	~~+++~~	~~2.43~~	~~3.87%~~	~~2.81±0.18~~
~~10%~~	~~+++~~	~~3.52~~	~~3.45%~~	~~3.62±0.25~~
~~20%~~	~~+++~~	~~5.94~~	~~2.38%~~	~~6.23±0.25~~

~~+++: No bloom, no bubbles, translucent, glossy, smooth.~~
~~*: The impact results were produced on notched test specimens with a non instrument controlled Charpy device and a 1 joule hammer and at a velocity of 2.9 m.s^{-1}.~~
~~For reference, the resilience of an unreinforced cast sheet and that of a cast sheet of commercial impact grade were measured, which have values of 1.35±0.03 kJ.mol^{-1} and 1.59±0.03 kJ.mol^{-1} respectively.~~

~~Figure 2:~~